

STUDY OF THERMODYNAMIC FACTORS FOR EQUILIBRIUM REACTIONS INVOLVED IN STEAM REFORMING OF NATURAL GAS

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We discuss the effect of different variables on steam reforming of natural gas to obtain hydrogen for use in fuel cells. The equilibrium compositions in the reformer are influenced by several factors: temperature, pressure, and the ratio of steam to methane (S/C) in the feed stream. We examine two equilibria: steam methane reforming and the water-gas shift reaction (conversion of water and carbon monoxide to carbon dioxide and hydrogen).

Key words: Steam reforming, methane, equilibrium, fuel cell.

Due to global concern about conserving natural resources and reducing environmental pollution, fuel cells are a promising technology to replace the conventional internal combustion engine for power production. The best fuel for efficient performance in low temperature fuel cells is pure hydrogen, since it simplifies system integration, maximizes system efficiency, and produces zero harmful emissions. However, hydrogen is not available in nature as a fuel, but rather is stored in hydrocarbon molecules. Therefore, hydrocarbon feedstock must be processed in order to extract hydrogen for stationary and portable fuel cell applications [1].

Hydrogen is produced industrially as a gas or a liquid by several methods. These methods include electrolysis of water, dissociation of ammonia, partial oxidation of hydrocarbons, and steam reforming of natural gas [2-8]. Removing carbon monoxide from a hydrogen-rich stream is a critical issue and an unavoidable problem when hydrocarbons or natural gas are used as the hydrogen source for fuel cells. Regardless of the reformer utilized, small amounts of carbon monoxide (CO), typically less than 1 mol%, must be removed to prevent poisoning of the fuel cell electrodes [9].

In designing a chemical reactor, in order to maximize the conversion and to get a first approximation for the composition of the output product streams and the feasibility of the process, the thermodynamic equilibrium of

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the chemical reactions involved must be considered. Other factors such as the reaction kinetics, heat transfer, the pressure drop, etc. must be taken into account. Optimization of the process usually is continued until close to equilibrium conversion values are achieved, at which point the reaction virtually stops.

This paper will examine two equilibrium reactions: steam methane reforming to form hydrogen and carbon monoxide, and the water-gas shift reaction with the carbon monoxide to form carbon dioxide. The feedstock will be just pure methane and water, not containing any reaction products. The equilibrium composition of the mixture will be calculated from equilibrium constants and initial partial pressures of the participants in the reaction.

Such reaction equilibrium studies are particularly useful when the amount of the catalyst used is enough to obtain concentrations close to the equilibrium values. This is a very common practice in the industry, where sufficient activity of the catalyst is assured when it is present in excess and the catalyst is spent vertically along the height of the reactor. Based on thermodynamic equilibrium, we can calculate the concentration of the individual components in the output stream of reaction products, quickly calculate the conversion for different reactions involved in the process, and assess the feasibility of the whole process without needing to calculate the reaction kinetics, heat exchange, or reactor geometry.

We examine the chemical reactions involved in the steam methane reforming process from the standpoint of thermodynamic equilibrium [10]. First we calculate the equilibrium constants starting from the process temperature and pressure [10]. The specific heat C_p for the different chemical species was calculated from the equation:

$$C_p = A + BT + CT^2$$

where A , B , C are constants; T is the absolute temperature, K.

The enthalpy was calculated based on the specific heats:

$$dH = C_p dT$$

where H is the enthalpy.

The van't Hoff equation was used to calculate the Gibbs free energy:

$$d\left(\frac{\Delta G}{RT}\right) = -\left(\frac{\Delta H}{RT^2}\right)dT$$

where G is the Gibbs energy; R is the universal gas constant.

Table 1

Components	Symbol	Conversion	Equilibrium concentration, moles
CH ₄	f	$-fx_a$	$f - fx_a$
H ₂ O	n	$-fx_a - fx_ax_b$	$n - fx_a(1 + fx_b)$
CO	c	$-fx_a - fx_ax_b$	$c + fx_a(1 - fx_b)$
CO ₂	d	fx_ax_b	$d + fx_ax_b$
H ₂	h	$3fx_a + fx_ax_b$	$h + fx_a(3 + x_b)$
Sum	$f + n + c + d + h$		$f + n + c + d + h + 2fx_a$

The relationship between the Gibbs free energy and the equilibrium constant K is expressed by the equation:

$$\ln K = -(\Delta G/RT)$$

The equilibrium constants can be found in tables [11] or calculated over a broad temperature range.

We define the conversion x as the ratio of the number of moles of a component consumed in the reaction to the initial number of moles of this component in the reactor feedstock [12]. The values of the conversion are within the range from 0 to 1, and indicate the extent of reaction.

Two reactions occur during steam reforming [13]. The first reaction (a) is steam reforming of methane, which converts methane to hydrogen and carbon monoxide:

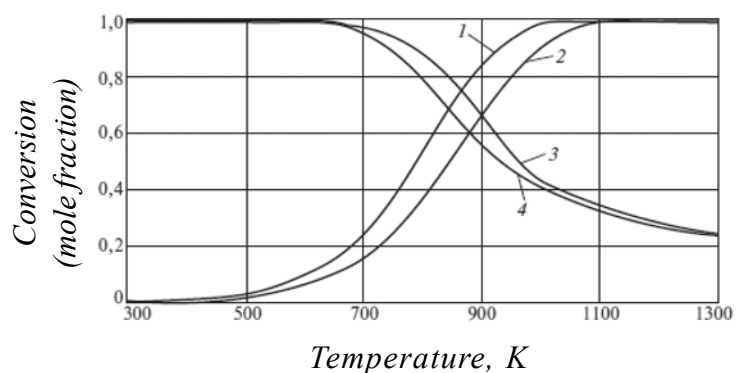


Fig. 1 Conversion vs. temperature and pressure (in degrees K) for steam:methane mole ratio equal to 3:1 ($S/C = 3$): 1) x_a ($P = 0.1$ MPa); 2) x_a ($P = 0.3$ MPa); 3) x_b ($P = 0.3$ MPa); 4) x_b ($P = 0.1$ MPa).

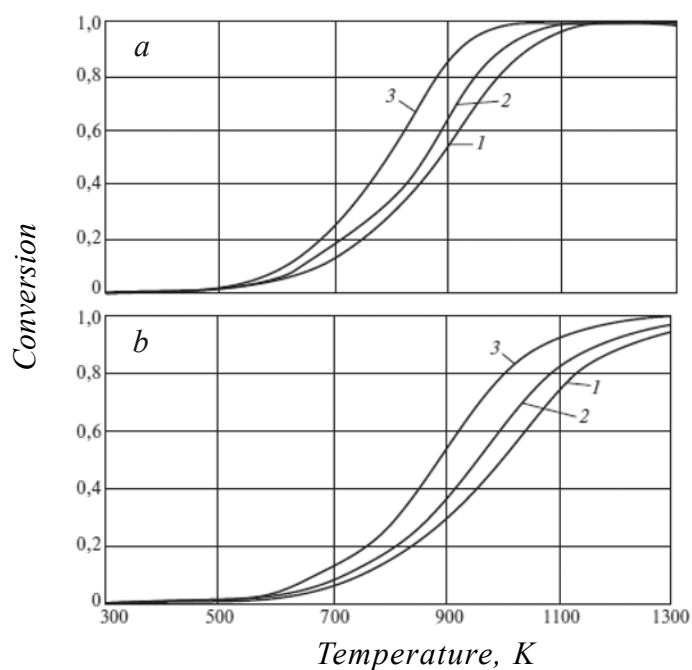


Fig. 2 Conversion for reaction a vs. temperature and pressure [1) 0.5 MPa); 2) 0.3 MPa); 3) 0.1 MPa] for steam:methane mole ratio (S/C): a) 3:1; b) 1:1.



The second reaction (*b*) is the water-gas shift reaction, leading to formation of carbon dioxide and more hydrogen [14]:



Table 1 gives the amount (in moles) of the participants in the reaction as a function of the conversion. In our case, the conversion for reaction *a* (x_a) is a function of the number of moles of methane, while the conversion for reaction *b* (x_b) is a function of the number of moles of carbon monoxide.

If we assume low-pressure ideal gas behavior, we can calculate to a good approximation the equilibrium constants for reactions *a* and *b* from these data:

$$Kp_a = \frac{P_{\text{CO}} P_{\text{H}_2}^3}{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}$$

$$Kp_b = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}}$$

where Kp_a , Kp_b are the equilibrium constants for reactions *a* and *b*; the P are the partial pressures of the components.

Using Raoult's law, which relates the partial pressures of the individual components to the total pressure, we transform the equations for calculating the equilibrium constants to the form:

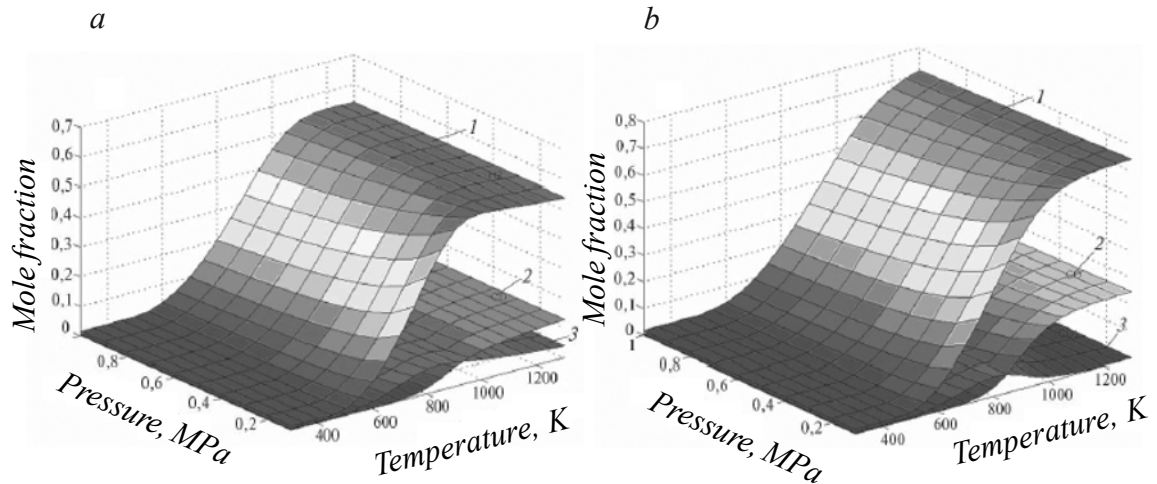


Fig. 3 Composition of reaction products for reaction *a* [1) hydrogen; 2) carbon monoxide; 3) carbon dioxide] vs. temperature and pressure for steam:methane ratio (S/C):
a) 3:1; b) 1:1.

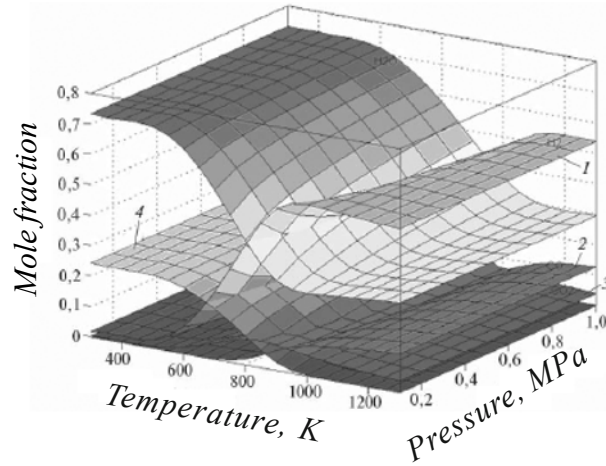


Fig. 4 Composition of reaction products for the overall reaction [1) hydrogen; 2) carbon monoxide; 3) carbon dioxide; 4) methane] vs. temperature and pressure for steam:methane ratio (S/C) equal to 3:1.

$$Kp_a = \frac{[c + fx_a(1 - x_b)][h + fx_a(3 + x_b)^3 P_T^2]}{(f + n + c + d + h + 2fx_a)^2 f(1 - x_a)[n - fx_a(1 + x_b)]}$$

$$Kp_b = \frac{fx_a x_b [h + fx_a(3 + x_b)]}{[c + fx_a(1 - x_b)][n - fx_a(1 + x_b)]}$$

where P_T is the pressure at temperature T .

Thus we have obtained two equations with two unknowns: x_a and x_b . To solve these equations, we used a Matlab® script for a numerical algorithm [15].

Reaction a is endothermic ($\Delta H_{298} = 205.7 \text{ kJ/mol}$) while reaction b is exothermic ($\Delta H_{298} = -41.2 \text{ kJ/mol}$). Thus an increase in temperature increases the equilibrium constant for reaction a and promotes formation of the products. The opposite occurs for reaction b. The conversion for reaction a increases with increasing temperature and decreases with increasing pressure, and consequently the optimal conditions for this reaction are low pressure and high temperature (Fig. 1).

Reformers generally operate within a range of steam:methane (S/C) mole ratios from 2:1 to 4:1 [6], so this factor is very important. Fig. 2a shows the conversion for reaction a vs. temperature and pressure for a steam:methane (S/C) mole ratio equal to 3:1, and Fig. 2b shows the same for a steam:methane (S/C) mole ratio equal to 1:1.

We see that for a steam:methane mole ratio equal to 3:1, the equilibrium conversion is higher, due to the increase in the partial pressure of the steam and the shift in the reaction equilibrium toward the products. Fig. 3 shows the effect of pressure, temperature, and the steam:methane mole ratio (S/C) on the composition of the reaction products for reaction a.

For the exothermic reaction b, we expect temperature and pressure to have the opposite effect: an increase in temperature will lead to a decrease in conversion, while an increase in pressure will lead to an increase in conversion. A decrease in the steam:methane ratio from 3:1 to 1:1 leads to a decrease in conversion.

Fig. 4 shows the equilibrium molar composition of the mixture of products from the overall reaction vs. temperature and pressure. We see that the concentration of hydrogen and carbon monoxide in the mixture increases with temperature over a certain time period, and then tends to stabilize. The effect of pressure is not very significant. The concentration of carbon dioxide reaches a maximum at an intermediate temperature, and then decreases. This maximum is due to the fact that the carbon dioxide is a product of reaction *a* and a starting reagent in reaction *b*, i.e., generally it is an intermediate.

When the steam:methane (S/C) ratio is low (1:1), the equilibrium mole fraction of hydrogen in the products is higher (because the water dilutes the unreacted hydrogen and other compounds), although the conversion of methane is lower. However, the downside is that the amount of carbon monoxide increases along with an increase in the amount of hydrogen. This is because the steam is almost completely consumed in the reaction with methane and can react only to a small extent with the carbon monoxide.

Therefore it is feasible to carry out the process at high temperature, which will form a large amount of hydrogen but with the disadvantage of increasing the concentration of carbon monoxide in the products. Usually this problem is remedied by adding a section to the reformer for carbon monoxide removal. It is also of interest to run the process at low pressure, although at high pressure the throughput of the reformer is improved and the reaction rate is increased. Nevertheless, at high pressure the thermodynamic equilibrium is limited and so the amount of hydrogen obtained is less than at low pressure. The steam:methane mole ratio is usually maintained at a compromise value of S/C = 3:1, since for low S/C coke can form and at high S/C the energy consumption for heating the steam dramatically increases.

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